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AN INVESTIGATION OF THE CROSSLINKING OF ETHYLENE-ACRYLIC ACID ESTER COPOLYMERS WITH SODIUM ALCOHOLATES USING MODEL COMPOUNDS

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ABSTRACT

As with ethylene–vinyl ester copolymers, crosslinking reactions are observed with ethylene–acrylic acid ester copolymers in the presence of sodium alcoholates. The reaction mechanism was examined by means of infrared spectroscopic characterization of the crosslinked products and kinetic measurements. In comparative investigations with methyl methacrylate polymers and sodium alcoholates, a reaction was not observed. This leads to the conclusion that the course of the reaction is determined by the hydrogen atom positioned alpha to the carbonyl group. When diethyl acetic acid ethyl ester (as the model substance) was reacted with sodium isopropylate, only isopropanol could be found by means of gas chromatography. Ethanol could not be detected, as it should have been in the case of ester condensation. Therefore, the crosslinking can be attributed to an aldol addition.

INTRODUCTION

While investigating the reactive compounding of ethylene-vinyl ester copolymers with ethylene-acrylic acid ester copolymers, we also studied the behavior of the ethylene-acrylic acid ester copolymerizates in the presence of sodium alcoholates. These copolymerizates were found to become crosslinked in the same way as the ethylene-vinyl ester copolymers; in particular, the ethylene-vinyl acetate copolymers [1].

Methods of crosslinking are known from the literature: peroxidic crosslinking [2, 3], which is the most common method for the vulcanization of homo- and copolymers of acrylic acid esters, and the production of ionomers by alkaline saponification [4]. In addition, a number of other substances have been found to induce crosslinking, e.g., sodium metasilicate [5], basic oxides or hydroxides of multivalent metals [6–8], and dibutyl stannic oxide [9]. The suitability of alkali metal alcoholates as crosslinking agents has not yet been described. This new reaction mechanism is the subject of this study.

EXPERIMENTAL

The crosslinking studies were performed in a polymer melt (Brabender Plasticorder) or in solution.

Copolymers of ethylene and ethyl acrylate were produced by the high-pressure process, with acrylic ester contents of 11.5 and 32 wt%. Low-molecular-weight polymethyl acrylate ($\overline{M}_n = 850$), polyethyl acrylate ($\overline{M}_n = 640$), and the model compound, diethyl acetic acid ethyl ester, were used to elucidate the reaction mechanism.

The low-molecular-weight acrylates were produced as follows: 1.88 mol toluene, 1.00 mol of the corresponding acrylate, 0.061 mol azobisisobutyronitrile, and 0.036 mol cumene were polymerized for 5 h at 80°C in a 1-L three-necked flask equipped with stirrer, gas inlet pipe (argon), and reflux condenser with a calcium chloride drying tube. The polymerizate was precipitated with cold petroleum ether. The substance was purified by double reprecipitation and subsequent drying to constant weight. The molecular weights of the polyacrylates were determined by a Knauer pressure osmometer.

Synthesis of Diethyl Acetic Acid Ethyl Ester

This substance was produced in four steps [10]:

1. Synthesis of diethyl malonic acid diethyl ester (I) by dialkylation of malonic acid diethyl ester by means of ethyl bromide.
2. Synthesis of diethyl malonic acid (II) from I by alkaline saponification in a mixture of ethanol and water.
3. Synthesis of diethyl acetic acid (III) by decarboxylation of II at temperatures between 160 and 170°C.
4. Synthesis of IV by azeotropic esterification of III with ethanol in the presence of tetrachloromethane and *p*-toluene sulfonic acid. Purification of IV by fractionation by using a 1.5-m packed column ("Braunschweiger Wendeln"). The equilibrium state was reached after 2.5 h. The main fraction distills over at a head temperature of 152.3 to 152.4°C; 100% purity (gas chromatography; IR, NMR, and mass spectra).

The alcohol-containing sodium alcoholates or their solutions in the corresponding alcohol were prepared by direct reaction of sodium with the respective alcohol. For example, 5 mL diethyl acetic acid ethyl ester was mixed with a solution of 8 mL sodium isopropylate in isopropanol (38.8 wt%) and boiled in an ampule for 8 h.

Alcohol-free sodium alcoholate was prepared by reacting a sodium dispersion in dry xylene with the stoichiometric amount of alcohol, followed by separation of xylene by distillation *in vacuo*.

A Brabender roller kneader type W 50 was used for studies in the polymer melt. The torque–time curves were recorded at 30 rpm.

The kinetic measurements were as follows: 20 mL of the corresponding polymer solution in toluene, with concentrations between 0.02 and 0.04 mol/L, was poured under argon into a dry 50 mL Erlenmeyer flask. After a tempering time of 15 min in the thermostat (usually up to about 40°C), 2 mL of the solution, with 0.03 to 0.05 mol/L NaOR in the corresponding alcohol, was syringed. The reaction was stopped by adding a mixture of 27 mL isopropanol and 3 mL water. Subsequently, NaOH formed from unreacted NaOR and water was titrated with 0.1 *N* hydrochloric acid versus phenolphthalein at ambient temperature.

The infrared spectra were obtained by means of a UR 10 Carl-Zeiss Jena, GDR spectrometer. The polymer solution (toluene) to be examined was dropped on a KBr plate. The solvent was then evaporated at 45°C in a drying oven. The KBr plates were stored for 24 h in a vacuum-drying oven at 45°C (3 torr) to remove the solvent completely. A thin polymer film was thus formed on the plate.

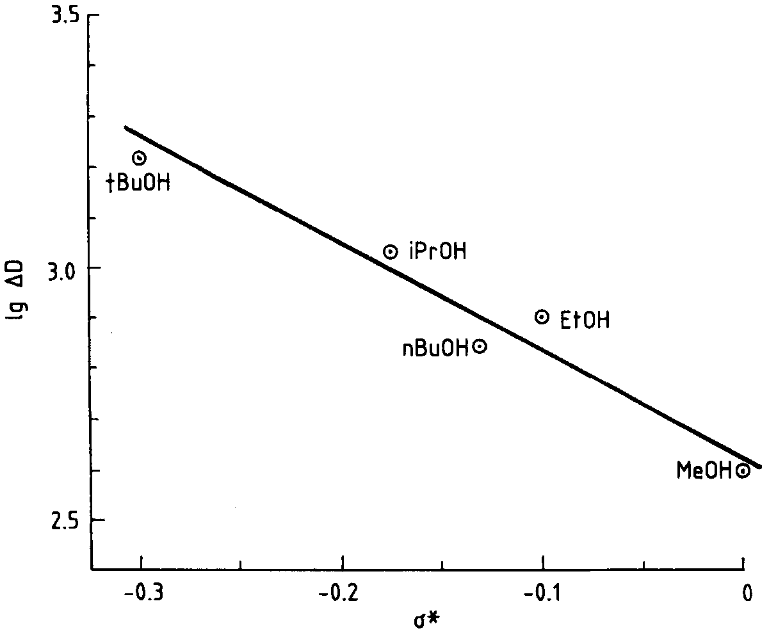


FIG. 1. Dependence of the torque increase after a reaction time of 2 min on the σ^* values of Taft. c_{NaOR} = 2 wt% (related to pure alcoholate). Ethyl acrylate content of the copolymer: 11.5 wt%. Kneader case temperature: 140°C.

RESULTS AND DISCUSSION

In the reaction of ethylene–ethyl acrylate copolymers with alcohol-containing sodium alcoholates in the polymer melt, the crosslinking rate increases with increasing alcoholate concentration, increasing ethyl acrylate content in the copolymer, and increasing reaction temperature [11, 12]. An increase in the crosslinking rate is also observed with decreasing electrophilic character of the alcohols in the alkoxides.

When recording the increase in torque (ΔD), reached 2 minutes after addition of the corresponding crosslinking agent to a copolymer melt in the Brabender Plastograph, versus the polarity constant σ^* of the corresponding alcohol, a dependence is obtained as shown by Fig. 1.

Since ethylene–ethyl acrylate copolymers are only slightly soluble in aromatic hydrocarbons at ambient temperature, the soluble low-molecular-weight homopolymerizates of acrylic acid methyl ester (PMA)

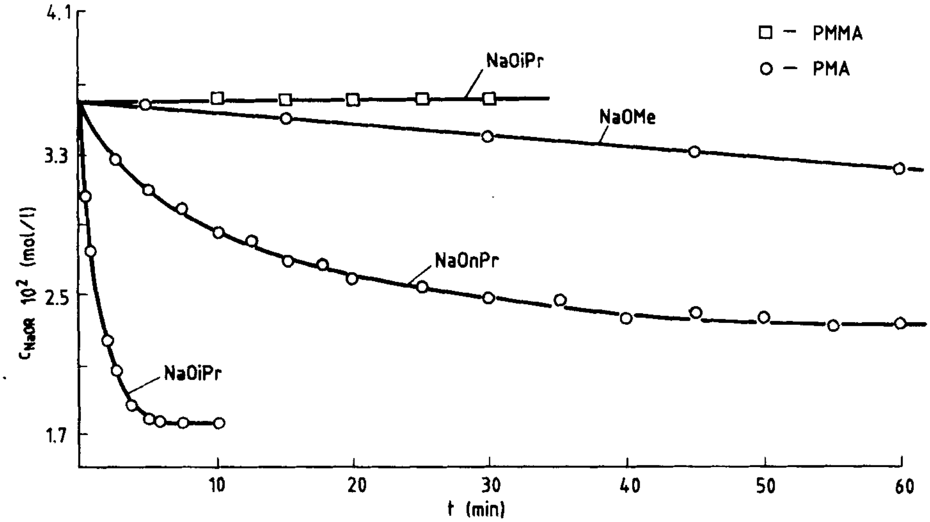


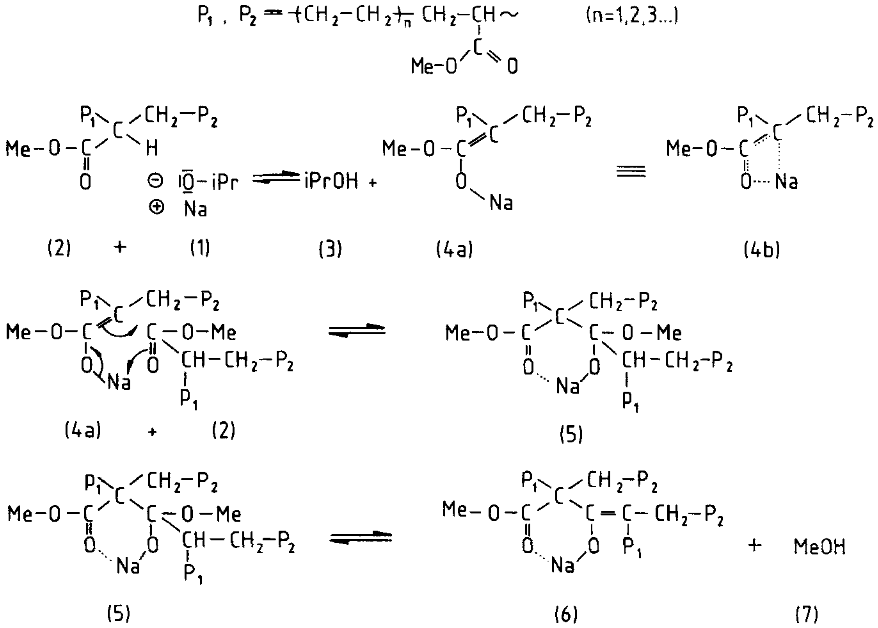
FIG. 2. NaOR consumption in dependence on reaction time $c^0_{NaOR} = c^0_{Polymer}$ = 0.036 mol/L. Solvent: Toluene. Temperature: 50°C.

and acrylic acid ethyl ester (PEA), as well as the model substance diethyl acetic ethyl ester, are used to investigate the crosslinking reaction. The precise mechanism can be deduced by combining both kinetic and nonkinetic methods of analysis.

Reactions of PMA in toluene solutions with sodium alcoholates in a rotation viscometer always increase the mixture's viscosity. The speed of the increase differs depending on the reaction conditions and the particular sodium alcoholate type. For comparison purposes, polymethyl methacrylate (PMMA) was reacted in toluene solutions. An increase in viscosity was not observed.

Preliminary tests showed that sodium alkoxide is completely converted in crosslinking of PMA. This is another indication of the fact that PMMA does not react with sodium alcoholates (NaOR). The unreacted alkoxide concentration was determined by titration with dilute hydrochloric acid.

Figure 2 represents the temporal change in concentration of different sodium alcoholates reacted with PMA and PMMA. The diagram shows that the reaction rate with PMA depends on the particular alcoholate. For PMMA, a decrease in the alkoxide concentration was not observed



SCHEME 1.

with sodium isopropylate. Obviously, a hydrogen atom at the α-carbon atom is necessary for the reaction.

Gas-chromatographic analysis of the reaction products of PMA with alcohol-free sodium isopropylate (NaOiPr) in toluene solution demonstrated that isopropanol is formed during the reaction. Methanol could not be found. Therefore, an ester condensation, as in Scheme 1, does not occur, as we had assumed earlier in Ref. 11.

The infrared spectra of slightly crosslinked but still soluble PMA samples (Fig. 3) differ from the spectrum of the parent substance only by the appearance of a new band at 1595 cm^{-1}.

This band is not due to the alcoholate still being included, since a definite dependence of the ratio of the bands at 1745 and 1595 cm^{-1} on the reaction time was found (Table 1). The band at 1745 cm^{-1} has to be assigned to the C=O valence vibration of the ester grouping. Its intensity decreases with increasing reaction time, while the intensity of the band at 1595 cm^{-1} increases.

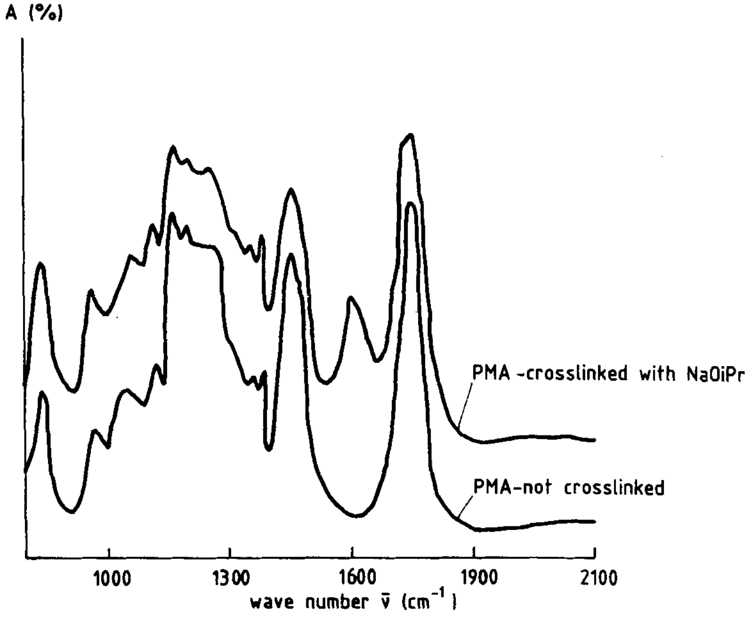
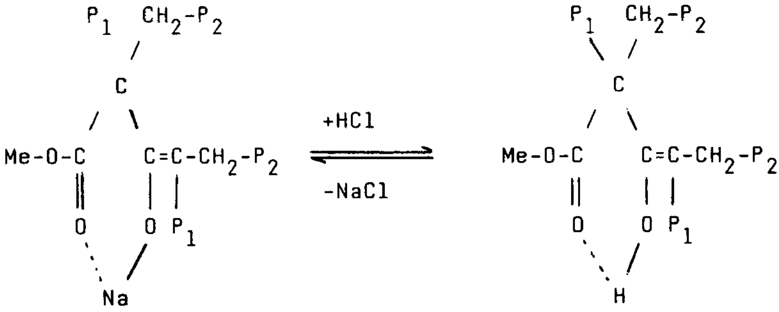


FIG. 3. Infrared partial spectra of samples not crosslinked and partly crosslinked with NaOiPr.

TABLE 1. Dependence of the Band Ratio on the Reaction Time

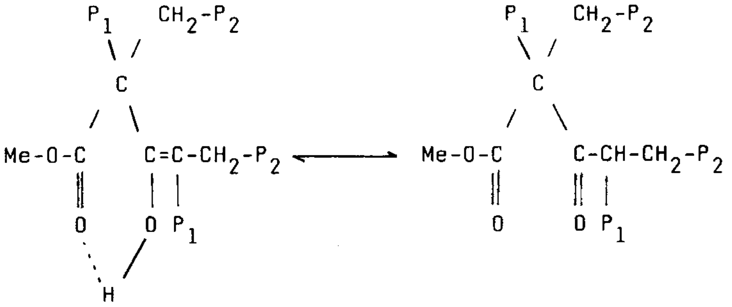
Reaction time *t*, min	Band height *h*, mm 1745 cm^{-1}	1595 cm^{-1}	Band ratio $\frac{h\,(1745\ cm^{-1})}{h\,(1595\ cm^{-1})}$
0	88.0	–	88.0
2	77.0	14.5	5.32
5	76.0	15.5	4.90
6	72.5	21.5	3.37
8	71.5	22.0	3.25

Supposing that, in contrast to the findings, condensation occurs with a splitting-off of methanol (7), the following should happen: The enolate formed (6) is converted with dilute acid to the corresponding enol (8):



(6) (8)

The enol is transformed to the keto form (9):



(8) (9)

due to the absence of resonance stabilization. If the band found in the infrared spectrum at 1595 cm^{-1} is to be assigned to an enolate grouping of structure (6), it should become smaller or disappear, after complete conversion, by treatment of the crosslinked sample with dilute hydrochloric acid. Two new bands should appear in the spectrum at 1720 and 1735 cm^{-1} due to a β-ketoester structure. Figure 4 shows that the band at 1595 cm^{-1}, typical for crosslinking, disappears after treatment of the sample with hydrochloric acid. However, new bands typical of β-ketoesters do not appear, and the infrared spectrum obtained is identical to the one of noncrosslinked PMA.

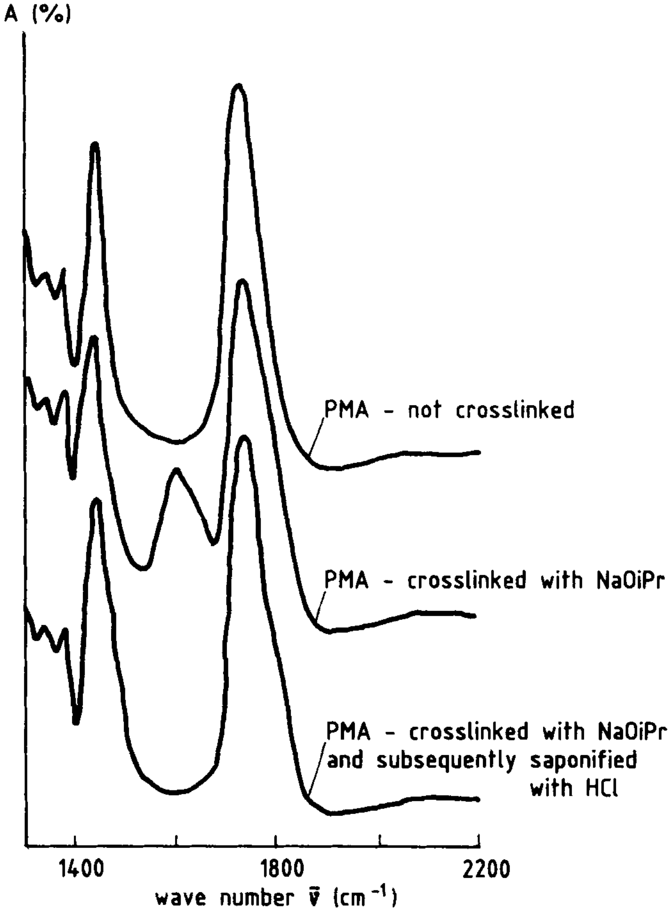


FIG. 4. Infrared partial spectra of samples not crosslinked, crosslinked with NaOiPr, and one crosslinked and treated with dilute hydrochloric acid.

The literature does not provide evidence that products of ester condensation can be again split into their starting components in acidic medium. Such reactions are only possible in alkaline medium. Therefore, the crosslinking cannot be attributed to a complete Claisen condensation. However, if crosslinking is initiated by the formation of the aldol addition product, a relatively fast reverse reaction to the starting components is possible in acidic medium.

Kinetic studies on the crosslinking reaction were performed with the model substance diethyl acetic acid ethyl ester (DAE) as well as low molecular weight PMA and PEA samples. The reaction order was determined by reacting a toluene solution of PEA with sodium isopropylate at 40°C.

Figure 5 demonstrates that the reaction obeys a second-order time law, which causes a straight line, while a plot according to the first or third order is characterized by a slight curvature. The application of different starting concentrations of the reactants permits determination of which time law is valid (Fig. 6):

$$v = k[\mathrm{NaOR}]^2$$

or

$$v = k[\mathrm{NaOR}][\mathrm{PEA}]$$

The linear correlation between the logarithm of the concentration ratio and the reaction time proves the validity of the rate law of the form

$$v = k[\mathrm{NaOR}][\mathrm{PEA}]$$

Investigations dealt not only with the dependence of the reaction rate on temperature and the nature of the solvent used, but also with the influence of the alkyl group of the alcohols contained in the alkoxides. The dependence is represented by Fig. 7, with PEA as an example. The reaction rate increases with increasing I effect or decreasing σ^* value, respectively, of the alkyl group of the corresponding alkoxide. A plot of the logarithm of the rate constants versus the corresponding σ^* values of Taft (Fig.8) proves the linear dependence. This is in agreement with the results obtained with the polymer melt. Hence, the reaction rate increases with decreasing electrophilic character of the alcohols in the alkoxides.

The rate constants for PMA were always higher under comparable reaction conditions. This is in line with the fact that activation energies are always lower for PMA (15.3 to 20.8 kcal/mol) than for PEA (17.8 to 23.6 kcal/mol). The reason can be found in the difference in steric hindrance of both the alkoxide attack on the proton of the carbon atom in the α-position and the aldol addition.

Reaction of DAE with pure sodium isopropylate yielded isopropanol

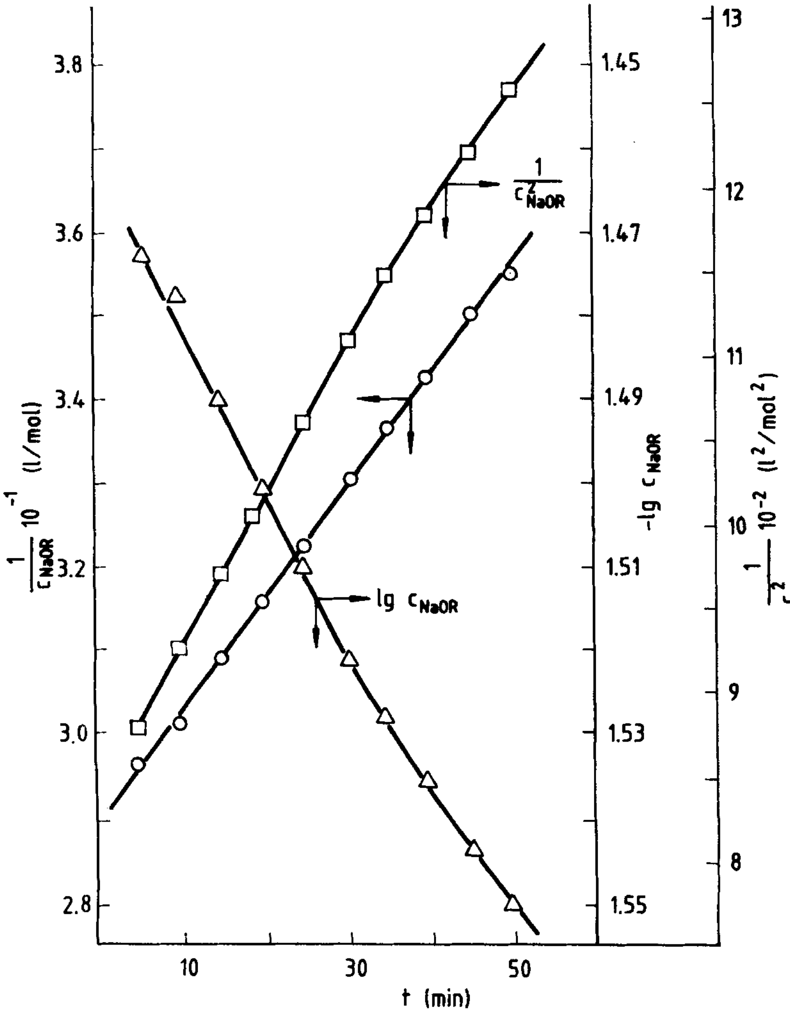


FIG. 5. Graphic evaluation of the measured results according to the time laws of first-, second-, and third-order. $c^0_{PEA} = c^0_{NaOiPr}$ = 0.036 mol/L. Solvent: Toluene. Temperature: 40°C.

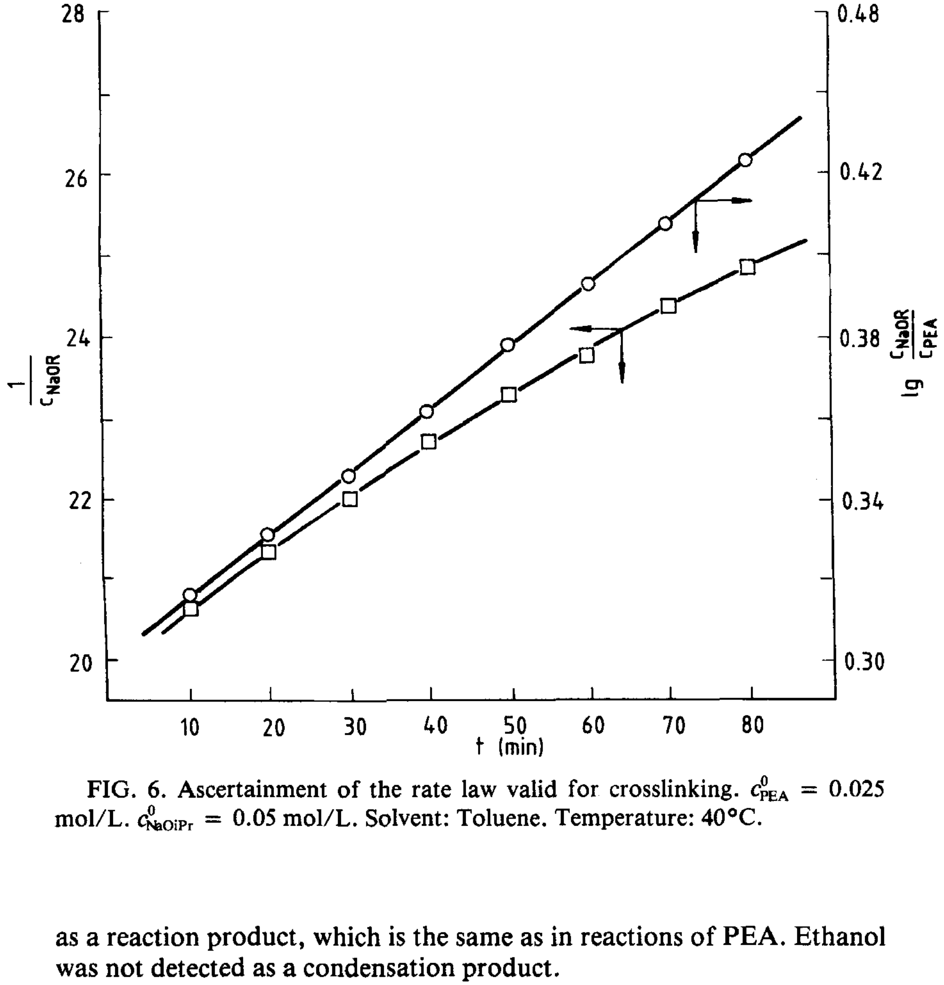


FIG. 6. Ascertainment of the rate law valid for crosslinking. c^0_{PEA} = 0.025 mol/L. c^0_{NaOiPr} = 0.05 mol/L. Solvent: Toluene. Temperature: 40°C.

as a reaction product, which is the same as in reactions of PEA. Ethanol was not detected as a condensation product.

A second-order rate law for the model substance was also found. This is a necessary, but not sufficient, condition for ascribing an identical mechanism to both the model and PEA. The activation parameters in Table 2 give additional information.

While the activation energies and enthalpies are in relatively good agreement, the activation entropy for the reaction of sodium *n*-propylate with the model substance is much more negative than the comparable value for PEA. Nevertheless, the activation parameters can be interpreted according to the same reaction scheme. This gives further support to

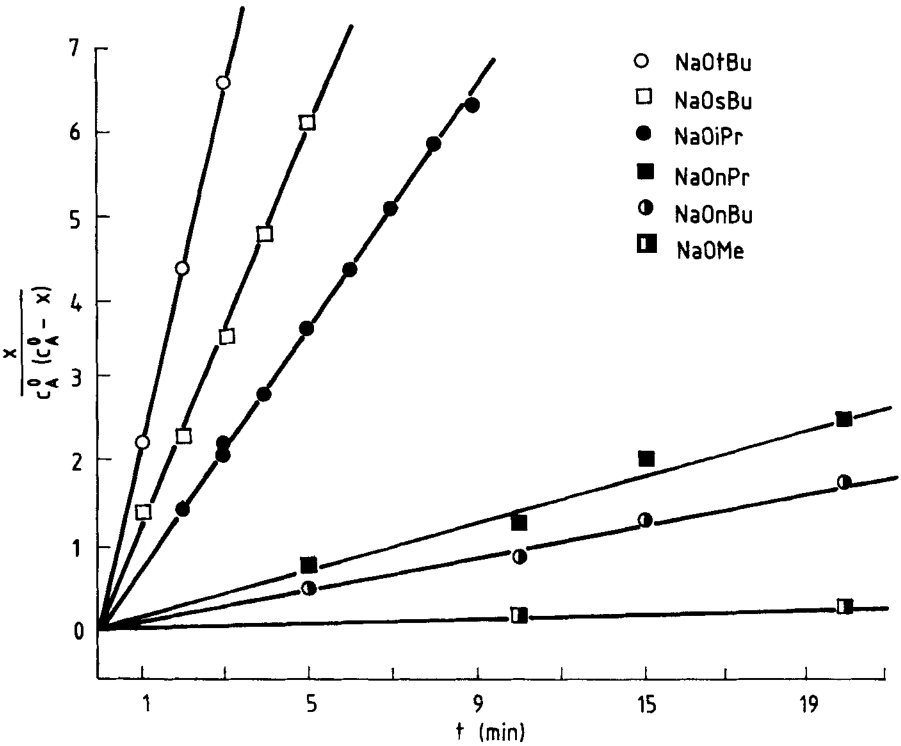


FIG. 7. Dependence of the reaction rate on the nature of sodium alcoholate. $c^0_{NaOR} = c^0_{PEA} = 0.036$ mol/L. Solvent: Toluene. Temperature: 40°C.

the assumption that the reactions of polyacrylates and the model substance proceed by the same mechanism.

Combination of the results obtained by means of kinetic and nonkinetic methods suggests the reaction mechanism of Scheme 2. It corresponds to the one described for EVA in Ref. 1.

The first reaction step involved formation of the sodium enolate of the polymer ester. The alcohol produced corresponds to the alkoxide used. This was demonstrated for the reaction of PMA with alcohol-free sodium isopropylate. The next equation shows different formulations of the compound (4a) produced in the first reaction step. Form (4) is preferred, which is in accordance with the most recent literature, while the formulations (4b) and (4c) are only mesomeric limiting structures of (4).

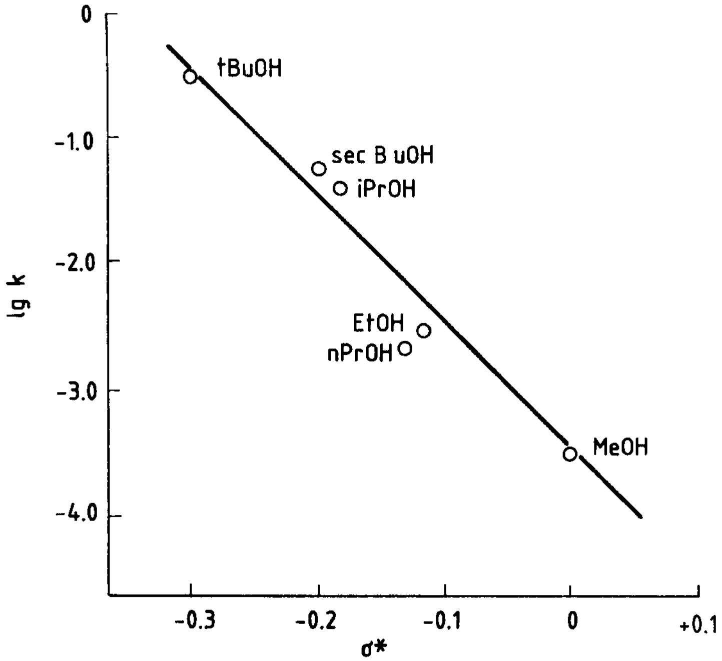
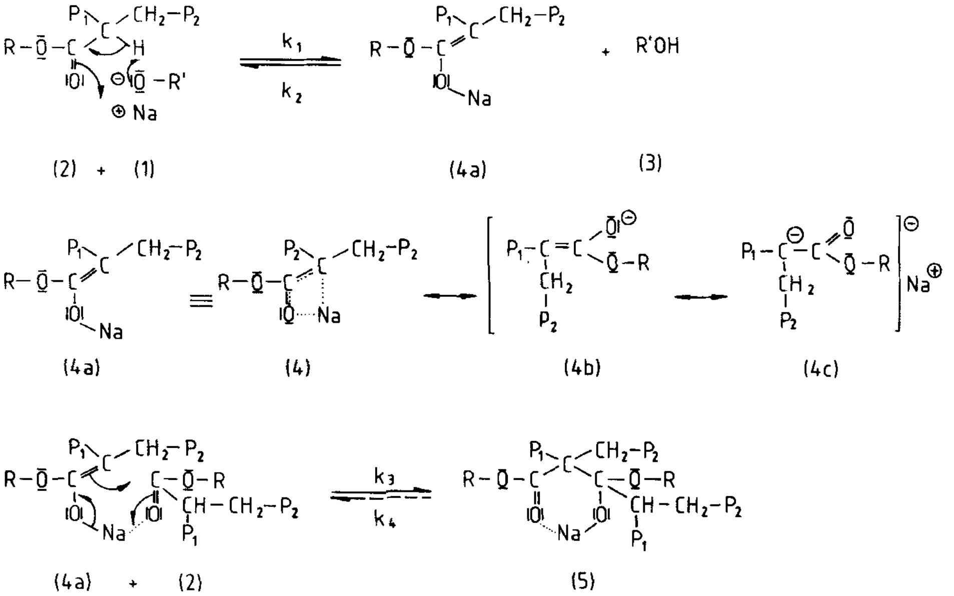


FIG. 8. Dependence on the rate constants on the δ*-values of Taft.

The carbonyl group of the ester component is coordinated to the compound's sodium cation (4a) in the second reaction step. Consequently, its polarization and, therefore, its reactivity are strengthened. The electron transfers proceed via a cyclic transition state, with the addition product (5) being stable in alkaline and neutral media. The proposed mechanism corresponds to an aldol addition in which product (5) is produced by crosslinking. The mechanism provides an easy explanation

TABLE 2. Activation Energies in Toluene for the Model Compounds

	E_A, kcal/mol	ΔH^*, kcal/mol	ΔS^*, kcal/mol
NaOiPr + DAE	18.6 ± 3.4	17.9 ± 3.4	−20 ± 3
NaOiPr + PEA	20.9 ± 1.0	20.3 ± 1.0	−6 ± 3



SCHEME 2.

of the instability of the crosslinked products in hydrolysis in acidic medium, and the nonappearance of a reaction with PMMA.

CONCLUSION

Investigations on the crosslinking mechanism of ethylene acrylic ester copolymers with sodium alcoholate are only practicable in a limited range due to the low solubility of the copolymerizates. For this reason, the model substances used were readily soluble low-molecular weight homopolymerizates of the acrylic methyl ester (PMA), the acrylic ethyl ester (PEA), and diethyl acetic ethyl ester (DAE). They obey the second reaction order and a rate law of the form

$$v = k[\mathrm{NaOR}][\mathrm{polyacrylate}]$$

The reaction rate increases with decreasing σ^* value of the alkyl group of the corresponding alkoxide. Under comparable reaction conditions, PMA will always result in higher rate constants than PEA. Consequently, activation energies for PMA are always lower than those for PEA.

The crosslinking mechanism can be interpreted by combining kinetic and nonkinetic methods. The proposed mechanism corresponds to an aldol addition. The crosslinked products are unstable in acidic media.

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